

# Solvation of the Excited States of Chromophores in Polarizable Environment: Orbital Relaxation versus Polarization<sup>†</sup>

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A hybrid quantum mechanics/molecular mechanics (QM/MM) method for the electronic excited states has been developed. The equation-of-motion coupled cluster with single and double excitations method (EOM-CCSD) is used for the QM region, while the effective fragment potential (EFP) method describes a MM part. The EFP method overcomes the most significant limitation of QM/MM by replacing empirical MM interactions and QM/MM coupling by parameter-free first-principles-based ones, while retaining the computational efficiency of QM/MM. The developed QM/MM scheme involves quantum-mechanical coupling of the electrostatic and polarization terms in the QM/MM Hamiltonian and allows accurate calculation of the electronic excited states of chromophores in various environments. Applications to the water complexes of formaldehyde and *p*-nitroaniline show that the orbital relaxation of the solute in the electric field of the solvent provides the majority of the solvatochromic effect, and the response of the polarizable environment to the density of the specific electronic state is much smaller in magnitude.

## 1. Introduction

Differential solvation of the electronic states of a chromophore in a solvent, called solvatochromism, can be used as a measure of solute–solvent interactions.<sup>1,2</sup> While multiple absorption and emission spectroscopic studies provide valuable information on the magnitude and dynamics of solute–solvent coupling, calculations in the condensed phase still remain a major challenge to the theoretical community.<sup>3</sup> The increased number of nuclear and electronic degrees of freedom makes accurate ab initio calculations on a condensed phase system unfeasible long before the system can approach the bulk. One general approach to this type of problem is to separate a system into two parts, such that one (active) part is treated by quantum mechanical (QM) techniques, and the other, usually larger, part is calculated by using classical (molecular) mechanics (MM).<sup>4</sup> The Hamiltonian of the system then consists of three terms:

$$\hat{H} = \hat{H}_{\text{QM}} + \hat{H}_{\text{MM}} + \hat{H}_{\text{QM/MM}} \quad (1)$$

where  $H_{\text{QM/MM}}$  is a coupling term. Separation of the QM and MM subsystems, in principle, allows one to use any level of theory in both the QM and MM parts.

There are an increasing number of studies devoted to description of the electronic spectroscopy in the condensed phase.<sup>5–16</sup> For example, electronic excited states of solutes have been extensively studied by using dielectric continuum methods.<sup>5–7,11,13,14,17</sup> Although continuum models are computationally inexpensive, they cannot describe explicit solvent–solute interactions such as hydrogen bonding. Another promising approach for studying electronic spectroscopy in large molecular systems is by using fragment-based techniques such as the fragment molecular orbital method.<sup>18–22</sup> Polarizable QM/MM models for electronic excited states have been developed in

several groups,<sup>16,23–27</sup> starting by pioneering work of Warshel and co-workers who used the Langevin dipole solvent model.<sup>28,29</sup>

Traditionally, the MM part in QM/MM is included through parametrized force fields. A major drawback of such an approach is the dependence on fitted parameters for a chosen force field, such that different parametrizations may be optimal for different problems and the best parameters are often not well-defined. There is also a concern regarding the absence of short-range repulsion and dispersion, and often polarization coupling in the QM/MM term, although these issues have not been well studied.<sup>3</sup>

In order to overcome these drawbacks, the effective fragment potential (EFP) method<sup>30,31</sup> is used for the MM part. In the EFP, each solvent molecule is represented by an effective fragment (EF) with a set of parameters determined from a preparatory ab initio calculation. The uniqueness of the EFP method is that *all EFP force field parameters are derived from first principles*, that is, the method is free of parameter fitting. The EFP interaction energy is a sum of electrostatic (or Coulomb), polarization (or induction), dispersion, and exchange-repulsion terms. Through its force field, the EFP fragments can interact with each other and with ab initio components. It has been shown that EFP reproduces structures and binding energies in hydrogen- and  $\pi$ -bonded systems with an accuracy similar or in some cases even better, than that of the second-order Moller–Plesset perturbation theory, MP2.<sup>32–34</sup> Moreover, in order to improve accuracy and extend applicability of the EFP method to strongly interacting species (e.g., polar or ionic fragments), ab initio-derived short-range screening functions for the electrostatic, polarization, and dispersion terms have been introduced.<sup>32,35</sup> Recently, EFP1 water potential was combined with configuration interaction singles (CIS) and time-dependent density functional (TD-DFT) methods to model absorption spectra of chromophores in water.<sup>36,37</sup>

This work describes development of the hybrid QM/MM method for the electronic excited states, in which the equation-of-motion coupled-cluster with single and double excitations<sup>38–40</sup> (EOM-CCSD) method is used for the QM region and the

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effective fragment potential method describes the MM part. This QM/MM scheme has been implemented in the Q-Chem<sup>41</sup> electronic structure package; details of the EFP implementation in Q-Chem will be reported elsewhere.<sup>42,43</sup> Accuracy of the developed EOM-CCSD/EFP scheme is analyzed on examples of the electronic excitations in the formaldehyde–water and *p*-nitroaniline–water complexes.

## 2. Theory

**a. Effective Fragment Potential Method.** There are four interaction terms in the general EFP model potential (general EFP potential has been originally called EFP2 to be distinguished from the water potential EFP1<sup>30,44</sup>), each of which may be thought of as a truncated expansion: Coulombic (electrostatic), induction (polarization), exchange repulsion, and dispersion (van der Waals):

$$E^{\text{EFP-EFP}} = E_{\text{coul}} + E_{\text{pol}} + E_{\text{disp}} + E_{\text{exrep}} \quad (2)$$

The terms in the EFP potential may be grouped into long-range,  $(1/R)^n$  distance-dependent, and short-range interactions, which decay exponentially. The Coulombic, induction, and dispersion are long-range interactions, whereas the exchange repulsion and damping terms are short-range. EFP has been described in detail in several papers,<sup>30,31,45,46</sup> therefore only a brief overview of the terms will be presented below.

The Coulomb portion of the electrostatic interaction,  $E_{\text{coul}}$ , is obtained using the Stone distributed multipolar analysis.<sup>47,48</sup> This expansion is truncated at the octopole term. Atom centers and bond midpoints are used as expansion points. Classical Coulombic interactions become too repulsive at short-range, when the electronic densities of the interacting fragments overlap and charge-penetration effects play a role. To correct for these quantum effects, electrostatic interactions are moderated by an exponential screening term.<sup>32,35,49</sup>

Induction (polarization),  $E_{\text{pol}}$ , arises from the interaction of distributed induced dipoles on one fragment with static multipole field and a field due to induced dipoles on the other fragments. The polarizability expansion is truncated at the first (dipole) term; the molecular polarizability tensor is expressed as a tensor sum of anisotropic localized molecular orbital (LMO) polarizabilities. Therefore, the number of polarizability points is equal to the number of bonds and lone pairs in the system. The induction term is iterated to self-consistency, so it is able to capture some many body effects.<sup>50</sup>

Dispersion interactions are expressed by an inverse  $R$  expansion,

$$E_{\text{disp}} = \sum_n C_n R^{-n} \quad (3)$$

The first term in the expansion,  $n = 6$ , corresponds to the induced dipole–induced dipole (van der Waals) interactions. In EFP, coefficients  $C_6$  are derived from the (imaginary) frequency-dependent polarizabilities integrated over the entire frequency range.<sup>51,52</sup> Distributed (centered at LMOs) dynamic polarizability tensors are obtained using the time-dependent Hartree–Fock (HF) method. In addition, the contribution of the  $n = 8$  term is estimated as one-third of the  $n = 6$  term. Tang–Toennies damping is used to damp the dispersion interactions at short-range.<sup>53</sup>

The exchange repulsion interaction between two fragments is derived as an expansion in the intermolecular overlap,

truncated at the quadratic term.<sup>54–56</sup> Kinetic and overlap one-electron integrals are calculated between each pair of fragments on-the-fly. Thus, each effective fragment should carry a basis set and localized wave function, with the smallest recommended basis set being 6-31++G(d,p).<sup>57</sup>

**b. QM/EFP Scheme for the Ground State.** In a presence of the ab initio region, the Coulomb and polarization parts of the EFP potential contribute to the quantum Hamiltonian through additional one-electron terms:

$$\hat{H} = \hat{H}_0 + \langle p | \hat{V}^{\text{elec}} + \hat{V}^{\text{pol}} | q \rangle \quad (4)$$

Electrostatic contribution  $\hat{V}^{\text{elec}}$  to the Hamiltonian consists of four terms, originating from the electrostatic potential of the corresponding multipoles (charges, dipoles, quadrupoles, and octopoles). Polarization component  $\hat{V}^{\text{pol}}$  of the one-electron Hamiltonian consists of the potential due to induced dipoles of the effective fragments:

$$\hat{V}^{\text{pol}} = \frac{1}{2} \sum_k \sum_a^{x,y,z} \frac{(\mu_a^k + \tilde{\mu}_a^k) a}{R^3} \quad (5)$$

where  $\mu^k$  and  $\tilde{\mu}^k$  are the induced dipole and conjugated induced dipole at the distributed polarizability point  $k$ , and  $R$  and  $a$  are the distance and its  $x,y,z$  component between the polarizability point and the position of an electron. Summation in eq 5 comes over all polarizability points of all fragments. Thus, the wave function of the ab initio region depends on the values of the induced dipoles, which in turn depend on the magnitude of the static and induced fields due to other fragments and on the field created by the wave function:

$$\mu_b^k = \sum_a^{x,y,z} \alpha_{ba}^k F_a^{\text{total},k} \quad (6)$$

$$F^{\text{total},k} = F^{\text{mult},k} + F^{\text{ind},k} + F^{\text{ai},k} + F^{\text{nuc},k} \quad (7)$$

where  $\alpha_{ab}$  is the polarizability tensor,  $F^{\text{total}}$  is the total field at the polarizability point  $k$ ,  $F^{\text{mult}}$  and  $F^{\text{ind}}$  are fields due to static fragments' multipoles and induced dipoles, and  $F^{\text{ai}}$  and  $F^{\text{nuc}}$  are electronic and nuclear fields due to the quantum region. To satisfy the self-consistency requirements, a two-level iterative procedure is employed. At each iteration of the HF cycle, the induced dipoles of the effective fragments are iterated until self-consistency with each other and with the current wave function. As a result, upon convergence of HF, the obtained induced dipoles are consistent with each other and with the electronic wave function. The total polarization energy of the QM/MM system (at the HF level) is:

$$E_{\text{pol,gr}} = \frac{1}{2} \sum_a^{x,y,z} [-\mu_a^u (F_a^{\text{mult},k} + F_a^{\text{nuc},k}) + \tilde{\mu}_a^k F_a^{\text{ai},k}] \quad (8)$$

In the present EFP implementation, dispersion and exchange-repulsion interactions between the active (ab initio) region and the effective fragments are treated similarly to the fragment–fragment interactions, as additive corrections to the total energy. Thus, they do not affect the electronic excitation energies.

The total ground-state energy of the QM/EFP system is given as:

$$E_{\text{gr}}^{\text{QM/EFP}} = \langle \psi_{\text{gr}} | \hat{H}_0 + \hat{H}^{\text{elec}} + \hat{H}_{\text{gr}}^{\text{pol}} | \psi_{\text{gr}} \rangle + E_{\text{coul}} + E_{\text{pol,gr}} + E_{\text{disp}} + E_{\text{exrep}} \quad (9)$$

where  $\psi_{\text{gr}}$  is the ground state wave function,  $\hat{H}^{\text{elec}}$  and  $\hat{H}_{\text{gr}}^{\text{pol}}$  are electrostatic and polarization EF contributions to the Hamiltonian, and the subscript “gr” means that the induced dipoles corresponding to the electronic density of the ground state are used.  $E_{\text{coul}}$  is the electrostatic EFP-EFP energy;  $E_{\text{exrep}}$  and  $E_{\text{disp}}$  include the exchange-repulsion and dispersion energies of both EFP-EFP and ab initio-EFP regions, and  $E_{\text{pol,gr}}$  is the self-consistent ground state polarization energy of the QM/EFP system given in eq 8.

**c. EOM-CCSD/EFP Scheme for the Electronic Excited States.** In the EOM-CCSD/EFP calculations, the reference state CCSD equations for the  $T$  cluster amplitudes are solved with the HF Hamiltonian modified by electrostatic and polarization contributions from the effective fragments (eq 4). Induced dipoles of the fragments are kept unchanged during the coupled cluster iterations and are not reoptimized for the coupled-cluster wave function. This treatment is valid when the HF wave function is a good zero-order approximation to the coupled-cluster wave function and the electric fields created by these wave functions are similar. In this case, errors introduced by omitting the polarization self-consistency between the quantum and effective fragments’ regions can be neglected. For the systems considered in this work, these errors were estimated to be less than 0.001 eV.

The electronic excitation energies in EOM-CCSD are found from the eigenvalue problem:

$$\bar{H}R = ER \quad (10)$$

where  $\bar{H} = e^{-T}He^T$  is the similarity transformed Hamiltonian,  $T$  is the cluster operator (found from solving the CCSD equations for the reference state),  $R$  is the excitation operator, and  $E$  is the excitation energy.  $T$  and  $R$  operators are truncated at the second level, i.e.,  $T = T_1 + T_2$  and  $R = R_1 + R_2$ . The Davidson iterative procedure used to diagonalize the transformed Hamiltonian  $\bar{H}$  is solved with constant response of the EFP environment, that is, the induced dipoles of the effective fragments are kept at their “ground state” values. The QM/EFP excitation energy is then:

$$E_{\text{ex},1}^{\text{QM/EFP}} = \langle \psi_{\text{ex}} | \hat{H}_0 + \hat{H}^{\text{elec}} + \hat{H}_{\text{gr}}^{\text{pol}} | \psi_{\text{ex}} \rangle + E_{\text{coul}} + E_{\text{pol,gr}} + E_{\text{disp}} + E_{\text{exrep}} \quad (11)$$

where  $\psi_{\text{ex}} = e^T R \psi_{\text{gr}}$  is the excited state EOM-CCSD wave function.

To estimate a response of polarizable environment to the change of the electronic wave function upon excitation, the one-electron density of each excited state is calculated and used to obtain the EFP induced dipoles and polarization energy corresponding to the given electronic state  $E_{\text{pol,ex}}$ , resulting in the following equation:

$$E_{\text{ex},2}^{\text{QM/EFP}} = \langle \psi_{\text{ex}} | \hat{H}_0 + \hat{H}^{\text{elec}} + \hat{H}_{\text{gr}}^{\text{pol}} | \psi_{\text{ex}} \rangle + E_{\text{coul}} + E_{\text{pol,ex}} + E_{\text{exrep}} + E_{\text{disp}} \quad (12)$$

Polarization energy corresponding to these “excited state” induced dipoles  $\mu_{\text{ex}}^k$  and  $\tilde{\mu}_{\text{ex}}^k$  is:

$$E_{\text{pol,ex}} = \frac{1}{2} \sum_k \sum_a^{x,y,z} [-\mu_{\text{ex},a}^k (F_a^{\text{mult},k} + F_a^{\text{nuc},k}) + \tilde{\mu}_{\text{ex},a}^k F_{\text{ex},a}^{\text{ai},k}] \quad (13)$$

where  $F_{\text{ex}}^{\text{ai}}$  is the field due to the excited state one-electron density. Additional correction  $E_{\text{pol,corr}}$  to eq 12 should be added to account for the change in the  $\hat{H}_{\text{gr}}^{\text{pol}}$  upon excitation:

$$\Delta E_{\text{pol,corr}} = \langle \psi_{\text{ex}} | \hat{H}_{\text{ex}}^{\text{pol}} - \hat{H}_{\text{gr}}^{\text{pol}} | \psi_{\text{ex}} \rangle \cong -\frac{1}{2} \sum_k \sum_a^{x,y,z} [(\tilde{\mu}_{\text{ex},a}^k + \mu_{\text{ex},a}^k) - (\tilde{\mu}_{\text{gr},a}^k + \mu_{\text{gr},a}^k) F_{\text{ex},a}^{\text{ai},k}] \quad (14)$$

The last expression would be exact if the excited-state electronic wave function and the EFP induced dipoles were obtained self-consistently; otherwise it is an approximation only, providing, however, the leading contribution to the interaction of the excited state wave function with the ground-state induced dipoles.<sup>24</sup>

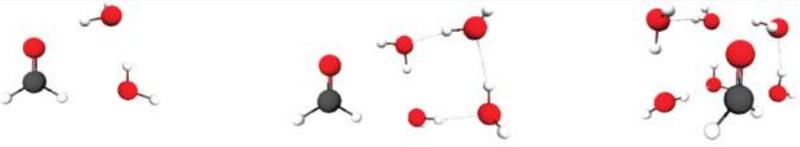
Combining eqs 8, 13, and 14, we arrive to the following expression:

$$\Delta E_{\text{pol}} = \frac{1}{2} \sum_k \sum_a^{x,y,z} [-(\mu_{\text{ex},a}^k - \mu_{\text{gr},a}^k) (F_a^{\text{mult},k} + F_a^{\text{nuc},k}) + (\tilde{\mu}_{\text{ex},a}^k F_{\text{ex},a}^{\text{ai},k} - \tilde{\mu}_{\text{gr},a}^k F_{\text{gr},a}^{\text{ai},k}) - (\mu_{\text{ex},a}^k + \tilde{\mu}_{\text{ex},a}^k - \mu_{\text{gr},a}^k - \tilde{\mu}_{\text{gr},a}^k) F_{\text{ex},a}^{\text{ai},k}] \quad (15)$$

that describes the response of the polarizable environment to the given excited state.  $\Delta E_{\text{pol}}$  is added to the electronic excitation energy of the considered state. The first two terms in eq 15 correspond to the difference of the polarization energy of the QM/EFP system in the excited and ground electronic states; the last term is the leading correction to the interaction of the ground-state-optimized induced dipoles with the wave function of the excited state.

The developed formalism for calculation of the electronic excitation energies in the hybrid QM/EFP system requires the knowledge of the one-particle excited-state density. In case of EOM-CCSD, where the Hamiltonian is non-Hermitian, the one-particle density matrix is obtained by subsequent solving right and left eigenvalue problems;<sup>58</sup> thus, the cost of the calculation is approximately doubled compared to the calculation of the excitation energy in the gas-phase. The cost of the calculation of the interaction energy of the EFP region is negligible compared to the cost of the excited state calculation.

The interface between EOM-CCSD and EFP can be easily extended to other excited state methods of the EOM-CC and configuration interaction (CI) family, such as CI with single excitations<sup>59,60</sup> [CIS] and with perturbative double excitations<sup>61,62</sup> [CIS(D)], or different variants of EOM-CC such as spin-flip,<sup>63–65</sup> electron attachment,<sup>66</sup> ionized potential<sup>67,68</sup> methods, or EOM-CCSD with inclusion of triple excitations.<sup>69,70</sup> Important advantage of the suggested EOM-CCSD/EFP scheme is that the electronic wave functions of the excited states remain orthogonal to each other since they are obtained with the same static characteristics of polarizable environment. This would not be the case if polarization of the environment were treated fully self-consistently and Davidson’s diagonalization procedure for the excited state were solved with instantaneous reoptimization of the induced dipoles of the solvent. The orthogonality between

TABLE 1: Solvatochromic Blue Shifts (eV) in the  $n \rightarrow \pi^*$  Transition in Formaldehyde–Water Complexes<sup>a</sup>


Full EOM-CCSD	0.146	0.103	0.284
EOM-CCSD/EFP	0.197	0.149	0.293
total indirect <sup>b</sup>	0.207	0.157	0.309
electrostatic <sup>c</sup>	0.173	0.125	0.262
polarization <sup>d</sup>	0.034	0.032	0.047
direct polarization <sup>e</sup>	-0.009	-0.008	-0.015

<sup>a</sup> Gas phase excitation energy is 4.137 eV. <sup>b</sup> Total (electrostatic + polarization) indirect contribution to the solvatochromic shift, see eqs 11. <sup>c</sup> Electrostatic (indirect) contribution to the solvatochromic shift (see text for details). <sup>d</sup> Indirect polarization contribution to the solvatochromic shift (see text for details). <sup>e</sup> Direct polarization contribution (i.e., “polarization correction”) to the solvatochromic shift calculated by eq 15.

the electronic states is necessary for calculation of the excited state properties such as transition densities and transition dipole moments. Another advantage of the developed EOM-CCSD/EFP scheme is the ability to obtain any number of the electronic excited states in one diagonalization cycle. Again, in case of self-consistent treatment of polarization, nonorthogonality of different electronic states could become an obstacle for simultaneously finding several states and requires separate Hamiltonian diagonalizations for each individual electronic state. As will be shown in Section 4, the magnitude of the polarization correction in the considered systems is of the order 0.01 eV and contains only a minor correction to the total solvatochromic shifts. This leads to a conclusion that the error due to nonself-consistent treatment of polarization is also very small and may be neglected in most practical applications.

Influence of the solvent on the electronic excited state can be separated into electronic and solvent reorganization effects. Although the electronic effects are important for modeling absorption or emission spectra (i.e., this situation would correspond to a nonequilibrium solvation), both electronic and solvent-reorganization effects have to be included for modeling equilibrium solvation. Typically, to account for solvent reorganization effects, one needs to follow the dynamics of the solvated state. The current implementation of QM/EFP aims at description of the instantaneous electronic solvent effects; description of the solvent reorganization effects on the excited state will be possible after implementing the analytic gradients within the QM/EFP scheme.

Although the developed QM/EFP scheme has multiple advantages for modeling electronic absorption spectra in solvents, certain limitations of its applicability should be mentioned. As any fragmentation technique, the QM/EFP scheme can be safely used when coupling between a solute and solvent region is relatively weak such that the electronic density of the solute and solvent can be separated. For example, QM/MM is generally not applicable for systems with delocalized electronic density (such as a nanotube or a conjugated polymer) since it is not possible to separate quantum and classical regions without breaking the conjugation. In cases when the electronic density of the solute is significantly spread to the solvent region, special care should be taken. For example, to properly describe the solvated electron<sup>71</sup> or charge-transfer-to-solvent states of halogens,<sup>72</sup> the quantum region should be extended to include several solvent molecules that host the electronic density of the

solute. On the other hand, excited states with Rydberg character may be described by the QM/EFP scheme either by increasing the quantum region or by introducing fully quantum short-range (exchange–repulsion and dispersion) coupling terms in the QM/MM Hamiltonian (see eq 9 and the preceding discussion). The quantum description of the short-range terms will properly account for cavity effects, which may be important in solvation of Rydberg states. This development is in progress and will be reported elsewhere.

### 3. Computational Details

All calculations are performed in GAMESS<sup>73,74</sup> and Q-Chem<sup>41</sup> electronic structure packages. The effective fragment potential for water molecule was generated with 6-311++G(3df,2p) basis<sup>75–77</sup> using MAKEFP run in GAMESS. Geometries of the formaldehyde and PNA complexes with two, four, and six waters were obtained as lowest energy structures found with Monte Carlo temperature annealing protocol. Geometries of these structures are provided in the Supporting Information. In Monte Carlo simulations, formaldehyde and PNA were also represented as effective fragments, with parameters obtained in 6-311++G(3df,2p) basis. The EFP parameters of water and geometries of the clusters were converted into Q-Chem format through a set of scripts.

6-31+G\* basis<sup>75,78</sup> is used for fully quantum and QM/MM calculations. In QM/MM calculations, formaldehyde or PNA are treated with EOM-CCSD, while waters are described by EFP. EOM-CCSD is used in fully quantum calculations. All orbitals were kept active in QM/MM calculations. Fully quantum EOM-CCSD calculations for complexes of PNA with two, four, and six waters were performed with frozen core orbitals in the correlated part of the calculations. EOM-CCSD calculations for gas-phase PNA were performed both with all active and with frozen core orbitals.

### 4. Results and Discussion

Table 1 compares the excitation energies of the  $n \rightarrow \pi^*$  transition in formaldehyde–water complexes obtained by the QM/MM (i.e., EOM-CCSD/EFP) and fully quantum approach, EOM-CCSD. Decrease of the dipole moment of formaldehyde upon excitation (EOM-CCSD values of the dipole moment in the ground and excited states are 2.65 and 1.40 D) results in more preferable solvation and stabilization of the ground state

TABLE 2: Solvatochromic Red Shifts (eV) in the  $\pi \rightarrow \pi^*$  Singlet and Triplet Transitions in PNA–Water Complexes


$\pi \rightarrow \pi^*$ singlet <sup>a</sup>			
Full EOM-CCSD <sup>b</sup>	-0.279	-0.193	-0.263
EOM-CCSD/EFP	-0.270	-0.195	-0.239
total indirect <sup>c</sup>	-0.262	-0.186	-0.220
electrostatic <sup>d</sup>	-0.213	-0.145	-0.177
polarization <sup>e</sup>	-0.049	-0.040	-0.043
direct polarization <sup>f</sup>	-0.008	-0.009	-0.019
$\pi \rightarrow \pi^*$ triplet <sup>a</sup>			
Full EOM <sup>b</sup>	-0.132	-0.087	-0.122
EOM-CCSD/EFP	-0.126	-0.088	-0.119
total indirect <sup>c</sup>	-0.124	-0.086	-0.115
electrostatic <sup>d</sup>	-0.098	-0.066	-0.094
polarization <sup>e</sup>	-0.026	-0.020	-0.021
direct polarization <sup>f</sup>	-0.002	-0.002	-0.004

<sup>a</sup> Gas phase excitation energies (with frozen-core orbitals in correlated calculations) are 4.654 eV (singlet) and 3.484 eV (triplet). Corresponding excitation energies with all-active orbitals differ by less than 0.001 eV. <sup>b</sup> Core orbitals were kept frozen in correlated calculations. <sup>c</sup> Total (electrostatic + polarization) indirect contribution to the solvatochromic shift, see eq 11. <sup>d</sup> Electrostatic (indirect) contribution to the solvatochromic shift (see text for details). <sup>e</sup> Indirect polarization contribution to the solvatochromic shift (see text for details). <sup>f</sup> Direct polarization contribution (i.e., “polarization correction”) to the solvatochromic shift calculated by eq 15.

with respect to the excited state in polar or polarizable solvents.<sup>15,26,79,80</sup> Thus, the blue solvatochromic shift is expected. As follows from Table 1, the blue shift of 0.1–0.3 eV is observed in formaldehyde complexes with 2, 4, and 6 waters. This shift is accurately captured by the EOM-CCSD/EFP scheme; small 0.01–0.05 eV discrepancies to full EOM-CCSD can be attributed to the incompleteness of the basis set and basis set superposition error in the full EOM-CCSD calculations, partial delocalization of the excited state on several waters that cannot be captured by QM/MM, and omission of the quantum treatment of the short-range terms, dispersion, and exchange-repulsion.

The main contribution to the solvatochromic shift in EOM-CCSD/EFP comes from the “indirect” term, consisting of electrostatic and polarization components of the EFP potential added as one-electron terms to the quantum Hamiltonian (see eq 11). The “indirect” term describes the orbital relaxation of the solute in a presence of the electrostatic field of the solvent. Approximate weights of the electrostatic and polarization components were estimated by performing additional calculation with omitting polarization from the water EFP potential. As follows from Table 1, the electrostatic contribution to the solvatochromic shift dominates the indirect term; polarization is responsible for about 20% of the shift. The response of the polarizable environment to the change in solute’s electronic density upon excitation, calculated by eq 15, is about three times smaller than the indirect polarization shift, or  $\sim 0.01$  eV in absolute values. Thus, polarization correction provides only a minor contribution to the solvatochromic shift in formaldehyde–

water complexes. As opposed to the indirect contribution, the direct polarization term stabilizes the excited state. It is expected to observe a somewhat larger role of polarization in larger clusters and bulk systems, where the many-body effects become very prominent. However, we expect that the trend where the relative weights of contributions to the solvatochromic shifts decrease in the order: electrostatic > indirect polarization > direct polarization, may be general to many polar or polarizable solvents.

Solvatochromic shifts of the charge-transfer (CT)  $\pi \rightarrow \pi^*$  singlet and triplet excitations in *p*-nitroaniline (PNA) are analyzed in Table 2. Shapes of the  $\pi$  and  $\pi^*$  orbitals are shown in Figure 1. The singlet CT excited state of PNA has zwitterionic character and a larger dipole moment (15.41 D in the excited state vs 7.38 D in the ground state, as calculated by EOM-CCSD). The zwitterionic excited state is stabilized in polar solvents and becomes red-shifted.<sup>81,82</sup> For example, the red shift of  $\sim 0.6$  eV is observed in bulk water.<sup>81</sup> As shown in Table 2, PNA clusters with 2, 4, and 6 waters experience the red shift of 0.2–0.3 eV. Comparison of the fully quantum and QM/MM treatments shows that the EOM-CCSD/EFP scheme captures the solvatochromic shifts very well, with discrepancies not exceeding 0.03 eV. Similarly to that in formaldehyde, the “indirect” term, that is, orbital relaxation of the solute in the electrostatic field of the solvent, is responsible for the majority of the shift in PNA, and the electrostatic term dominates here too, providing about 80% of the indirect contribution. The effect of repolarization of the environment as a response to a change of the electronic wave function in the excited state contributes

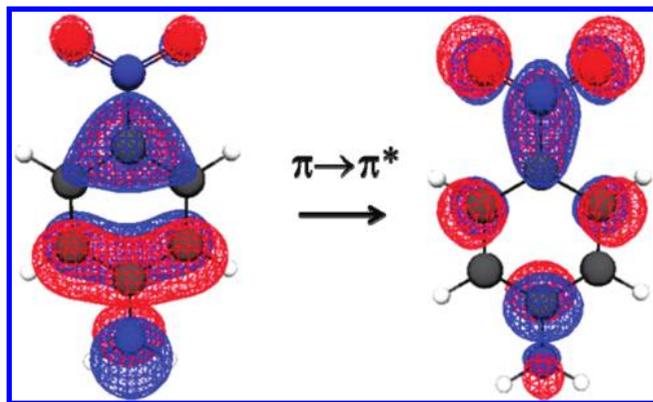


Figure 1. PNA  $\pi$  and  $\pi^*$  molecular orbitals.

3–8% to the total solvatochromic shift. Even though the effect of the polarization contribution is relatively small, it improves the agreement between the fully quantum and QM/MM calculations.

Solvatochromic shifts of the triplet  $\pi \rightarrow \pi^*$  transition in PNA are presented in the second part of Table 2. Analysis of the wave functions originated from placing two electrons in two orbitals shows that singlets can be either covalent or zwitterionic in character, whereas all triplets are covalent.<sup>83</sup> The covalent nature of the  $\pi \rightarrow \pi^*$  PNA triplet manifests itself in a relatively small increase in the dipole moment (10.39 D as compared to 7.38 D in the ground state), and, as a consequence, in smaller solvatochromic shifts of 0.09–0.13 eV. Relative weights of the direct and indirect terms and of the electrostatic and polarization contributions are similar to those in the singlet state. Theoretical investigation of the triplet states is especially important since triplets are usually not attainable by direct experimental measurements, but play an important role in relaxation dynamics of the electronic energy. Different solvation of the singlet and triplet states may explain observed differences in the relaxation dynamics of PNA in different solvents.<sup>82</sup> This important topic will be investigated in future work.

## 5. Conclusions

The interface of the effective fragment potential method and the EOM-CCSD excited state method has been developed. This QM/MM scheme involves quantum coupling of the electrostatic and polarization terms in the QM/MM Hamiltonian and allows accurate calculation of the electronic excited states of chromophores in various solvents. Computational cost of the developed method is about twice of the cost of the gas-phase EOM-CCSD calculations on a chromophore. Applications to the water complexes of formaldehyde and PNA show that the orbital relaxation of the solute in the field of the solvent provides the majority of the solvatochromic effect and is dominated by the contribution of the Coulomb term. Response of polarizable environment to the density of the specific electronic state is much smaller in magnitude.

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**Supporting Information Available:** Cartesian geometries of formaldehyde–water and PNA–water clusters are provided. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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